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Novel pre-treatments to control bromate formation during ozonation

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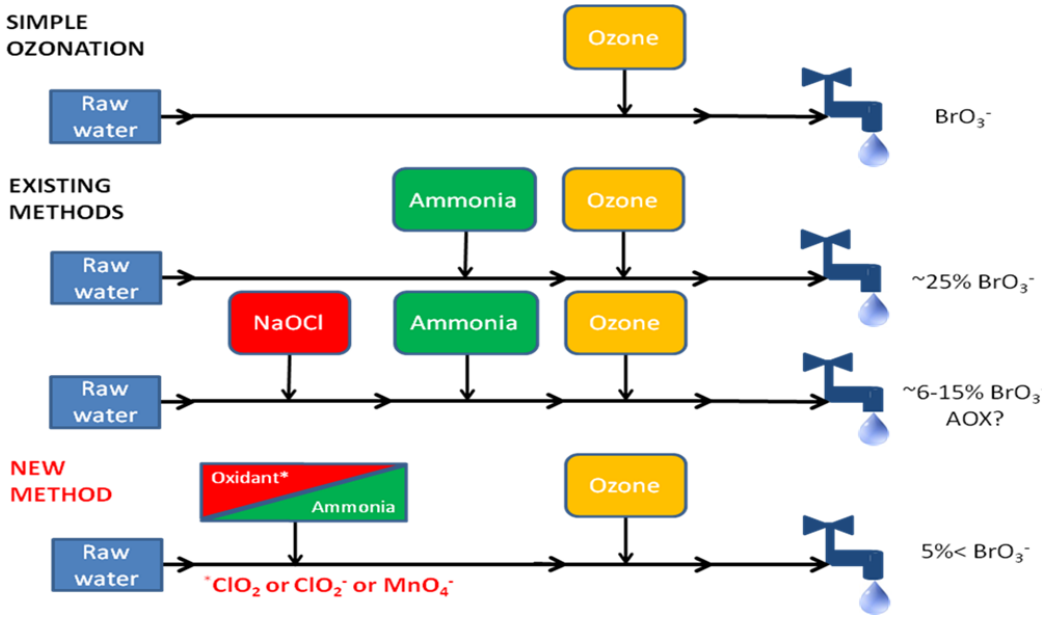
Highlights

- Pre-treatments were investigated which inhibit bromate formation in ozonation.
- ClO_2 and MnO_4^- with NH_4^+ were promising pre-treatments for bromate inhibition.
- Atrazine removal was only unaffected by the MnO_4^- with NH_4^+ pretreatment.
- MnO_4^- with NH_4^+ pre-treatments appears technical and economically feasible



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Abstract

Worldwide water shortage increase and water quality depletion from microbial and chemical compounds, pose significant challenges for today's water treatment industry. Both the development of new advanced oxidation technologies, but also the enhancement of existing conventional technologies is of high interest. This study tested improvements to conventional ozonation that reduce the formation of the oxidation-by-product bromate, while maintaining the effectiveness for removal emerging contaminants (atrazine). MnO_4^-, ClO_2^-, ClO_2, ClO^-, CH_3COOO^-, HSO_5^- or $S_2O_8^{-2}$ with NH_4^+ were tested as pre-treatments to ozonation of ground water. Each oxidant and NH_4^+ were added in a single stage or separately prior to ozonation. To the best of our knowledge, this is the first study that has tested all the above-mentioned oxidants for the same water matrix. Based on our results, the most promising pre-treatments were MnO_4^--NH_4^+, ClO_2^--NH_4^+ and ClO_2-NH_4^+. MnO_4^--NH_4^+ was the only pre-treatment that didn't inhibit atrazine removal. When compared with the previously proposed Cl_2/NH_4^+ pre-treatment, MnO_4^-+NH_4^+ was found as effective for preventing BrO_3^- formation, while atrazine removal was higher. In addition, MnO_4^-+NH_4^+ can be added in a single stage (compared to the 2 stage addition of Cl_2/NH_4^+) without causing the formation of potentially harmful chlorination-by-products.

Keywords: ammonia, atrazine, bromate, chlorine dioxide, ozone, permanganate

1. Introduction

The presence and subsequently the removal of emerging contaminants (ECs) like pesticides, hormones, medical drugs and naturally occurring toxic metabolites from water resources poses a challenge for the water industry [1-5]. In order to remove micropollutants in trace concentrations from water resources chemical oxidation technologies such as ozonation and advanced oxidation processes (AOPs) are increasingly applied in different types of source water [2, 6-12]. Ozone (O_3) is able to remove most ECs with less energy consumption than conventional UV/H_2O_2 AOPs [12-14], but at higher capital costs and with a larger footprint of the treatment unit. The recently developed UV/Cl_2 AOP appears to be a promising candidate for significantly reducing capital and operational costs for the oxidative removal of trace compounds especially from wastewater treatment plant effluents [15, 16].

Nevertheless, ozonation remains a preferred method for the removal of organic ECs as it is a simple to control and implement at existing waterworks. In addition to water purification, O_3 has been used for disinfection, taste, color, and odor removal, and the pre-oxidation of drinking water to reduce formation of byproducts in post treatment chlorination [17-19]. Ozone installations are currently found in many water treatment plants primarily for pathogen control and/or for taste and odor control such as the Metropolitan Water District of Southern California and Alameda County Water District in California [19]. This is because, O_3 readily reacts with unsaturated bonds in organic molecules through *cyclo* addition reactions leading to the formation of unstable ozonides that eventually breakdown to aldehydes and ketones. Its ability to form hydroxyl radicals ($HO^\bullet$) as a decomposition intermediate increases the oxidation efficiency of the technology by adding the possibility for non-selective oxidation [20]. A side effect of ozonation is the formation of bromate (BrO_3^-) when the source water contains naturally occurring bromide (Br^-) [17, 21-23]. Bromate is a probable human carcinogen [22, 24] and therefore its concentration is regulated in drinking water. BrO_3^- comprises the only ozonation by-product that is currently being regulated in drinking waters [18, 25, 26]. In the past, the drinking water standard limits for bromate have been decreased to 10.0 μg/L in Europe and in the USA (0.010 mg/L) [25, 26] and even stronger restrictions (5 μg/L) have been considered for its annual average concentration [26-28]. Following extensive evaluation of the risks and benefits of ozonation the USEPA decided against the reduction of the BrO_3^- limit because technical analyses indicated that many facilities utilizing ozonation for improved disinfection would be unable to meet the stringent disinfection criteria under LT2ESWTR and maintain bromate formation below 0.005 mg/L, at the same time. This applies especially for facilities were chlorine-resistant microorganisms such as *Cryptosporidium* necessitate treatment [19, 26, 28, 29].

The process in which BrO_3^- is formed during ozonation consists of two phases: a quick and a slow initiated by $HO^\bullet$ and O_3 respectively [30]. These mechanistic steps have been extensively studied and unveiled by von Gunten's research group and have been illustrated as a series of bimolecular reactions (Figure 1) [8, 30, 31]. The 4 major steps that lead to BrO_3^- formation begin with O_3 oxidizing bromide (Br^-) to hypobromite (BrO^-) or hypobromous acid (HBrO), depending on the solution pH. Then, HBrO/OBr^- is oxidized by $HO^\bullet$ to $BrO^\bullet$, followed by a disproportionation reaction ($2BrO^\bullet \rightarrow BrO^- + BrO_2^-$) to give BrO_2^- and finally O_3 oxidizes the latter ion to BrO_3^- [8]. A secondary pathway where $HO^\bullet$ oxidizes bromide to its corresponding radical ($Br^\bullet$), that either reacts with O_3 or $HO^\bullet$ to form $BrO^\bullet$ or HOBr/BrO^-, respectively has also been reported. The oxidation of HBrO/BrO^- can also occur with O_3 but at lower rates [8]. Identification of the mechanistic steps of BrO_3^- formation was crucial because it revealed its rate limiting steps and consequently assisted in adopting practices that can significantly reduce BrO_3^- formation.

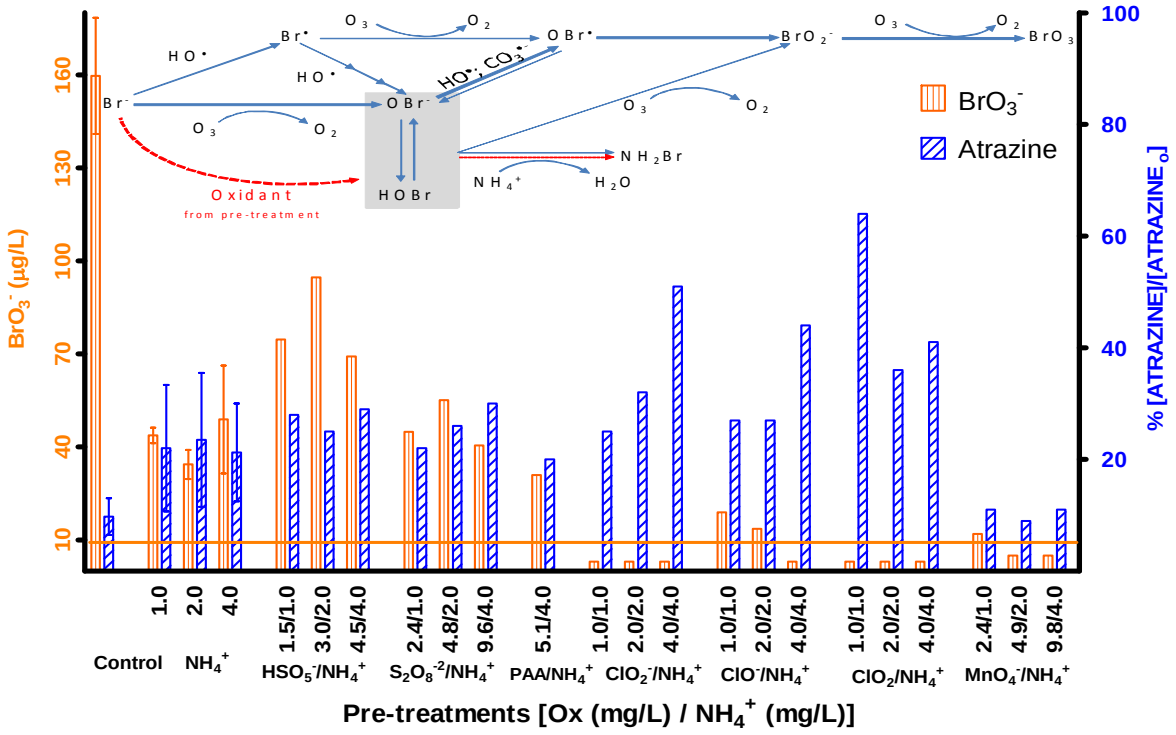

Figure 1: Effect of pre-treatment reagent pairs and concentrations [Oxidant (mg/L)/NH_4^+ (mg/L)] on BrO_3^- formation (left axis) and remaining atrazine (right axis) during ozonation. Experimental conditions: O_3= 3.5 mg/L; Br^- = 100 µg/L; $Atrazine_o$= 200 µg/L; NH_4^+ = 1.0, 2.0, 4.0, mg/L; [NH_4^+]/[Br^-] = 44, 88, 178; [Ox] =15, 30, 60 µM; [Ox]/[Br^-] = 12, 24,48; pH= 7.0. (Methods std error: SE_{BrO3-} = 4.5 µg/L; SE_{ATR}= 1.5 µg/L). Schematic inside Figure 1 is based on the mechanism discussed by [8, 53] and edited to include the effect of pre-treatments.

Based on this mechanistic understanding, several methods have been proposed to alter the water chemistry of the treated water in order to decrease the formation of bromate during the ozonation process. Depression of water pH to 6 shifts the equilibrium of HBrO/BrO^- towards HBrO which reacts slowly with O_3 to form BrO_3^-, therefore BrO_3^- formation is hindered [31, 32]. This pre-treatment has successfully and cost-effectively been applied in water facilities [19]. However if the treated water has moderate to high alkalinity (ground-water) the pH adjustment cost may be prohibitive reaching 2 to 9 times ozone's operational cost [27, 28]. Another method is the Cl_2/NH_4^+ pre-treatment [31]. Cl_2 is added prior to ozonation and oxidizes Br^- to HBrO/BrO^-, which then reacts with added NH_4^+ to form bromamine (NH_2Br, $k_{NH4+/O3}$=8 x10^7 $M^{-1}s^{-1}$) [8, 27, 28, 30, 31]. Since the latter molecule is not significantly oxidized by O_3 ($k_{NH2Br/O3}$=40 $M^{-1}s^{-1}$) [28], BrO_3^- formation is greatly reduced. However, this approach has some disadvantages including the formation of undesired chlorination by-products from the reaction of the added chlorine with organic matter and the need for sequential addition of Cl_2 and NH_4^+ since these

chemicals readily react with each other to form chloramines. The most recently tested technology, is the coupling of photocatalysis to ozonation, which besides causing acceleration of the degradation rates of ECs, it can also limit bromate formation [33]. The effectiveness of these pre-treatments greatly depends on the quality of the treated water, including pH, NOM and alkalinity since they affect the oxidation routes followed and contact times of O_3 or $HO^{\bullet}$ [28, 31, 34].

In our earlier study, [34], the abovementioned pre-treatments were evaluated for their efficiency to inhibit bromate formation while achieving one log atrazine (herbicide) removal from Br^- spiked ground water from the DTU (Technical University of Denmark) Campus, which has high alkalinity (HCO_3^-=332 mg/L, pH_o= 7.4) and a considerable concentration of 'aged' natural organic matter (NOM; DOC ~ 2.5 mg/L) [34]. This water presents an exceptional challenge for O_3 treatment because both O_3 and HO• are consumed by the NOM and high alkalinity, and consequently the required O_3 dose for contaminant degradation is significantly increased along with BrO_3^- formation [35]. Our previous results indicated that a high O_3 dose (3.5 mg/L) was needed to achieve 90% removal of atrazine from ground-water resulting in the formation of 130-170 μg/L BrO_3^-. The O_3-dose required to remove atrazine was unaffected even when ozone was applied as peroxone (O_3/H_2O_2 1:3.5 w/w), though it limited BrO_3^- formation below the drinking water limit of 10 μg/L. Depression of pH to 6 was proven insufficient to control BrO_3^- formation below the 10 μg/L limit in the ground water from the DTU Campus. Pretreatment with Cl_2/ NH_4^+ reduced BrO_3^- formation close to the 10 μg/L limit; however, atrazine removal was reduced to below 75%.

Based on the above, this co-operative study between Siemens Water Technologies and DTU aimed to investigate the efficiency of several oxidants commonly used in water treatment as replacements of Cl_2 in the "Cl_2/NH_4^+" pre-treatment for inhibiting BrO_3^- formation during ozonation to exceed the limit of 10 μg/L. It was anticipated that these alternatives may be advantageous to Cl_2, since they do not form chlororganic byproducts nor react directly with NH_4^+. Therefore, sodium hypochlorite (NaClO) [22, 36] and chlorine dioxide (ClO_2) [21, 32], and the never before tested paracetic acid (CH_3COOOH, PAA), potassium persulfate ($K_2S_2O_8$), peroxymonosulfate ($KHSO_5$), and potassium permanganate ($KMnO_4$) were used in this study. Apart from monitoring BrO_3^- formation for each pre-treatment, the effect of the concentration of the oxidant and NH_4^+ added were investigated. Also, the extent to which these pre-treatment affected atrazine removal during ozonation, was monitored. Atrazine was chosen as the model EC of this study, because it is a common treatment target for ozonation and its degradation is mainly attributed to the $HO^{\bullet}$ formed during ozonation and less on direct ozonation [4, 12, 34, 37, 38]. In addition atrazine is part of the list of contaminants that the Water Framework Directive requires to be monitored in surface waters and its maximum allowable concentration in surface waters should not exceed 2.0 μg/L [39]. To the best of our knowledge, this is the first study that investigates the potential use of all these oxidants on the same source water, in order to control BrO_3^- formation during ozonation under the 10 μg/L limit, while achieving at the same one log atrazine removal.

2. Materials and Methods

2.1 Reagents:

Atrazine (ATR), sodium bromide (NaBr), potassium permanganate ($KMnO_4$), sodium chlorite ($NaClO_2$), sodium hypochlorite (NaClO), paracetic acid (CH_3COOOH), peroxymonosulfate ($KHSO_5$), and potassium persulfate ($K_2S_2O_8$) were purchased from Sigma-Aldrich and used as received. The treated tap water was first pH adjusted to 7 and then spiked with atrazine and Br^- with final concentrations of 200 μg/L and 100 μg/L, respectively. Details on the preparation of the water mixture and chlorine dioxide (ClO_2) stock solution are found in Antoniou and Andersen (2012) [34]. Details on the chemical composition of the DTU-tap water are found in Table S1.

2.2 Batch Experiments:

In 120 mL blue cap borosilicate glass bottles, 100 mL of the water mixture were added and placed in a water bath at 15°C. For the pre-treatment experiments, the oxidant was added first, allowing 15 min reaction time, NH_4^+ (as NH_4SO_4) was added next and allowed another 15 min of reaction time, before O_3 addition (2 stages addition). For single stage addition, both the oxidant and NH_4^+ were added at the same time 30 min before O_3. Specific aliquots from the O_3 stock solution were added and the bottles were left in a water bath to react overnight, at T=15°C. The half-life of 1.7 mg/L O_3 in the same water matrix was measured at 2.74 min, which means enough time was given for the reaction to be completed (estimated O_3 contact time of 30 min) [34]. Samples were taken the next day for the analysis of BrO_3^- and ATR. The error bars in the Figures represent the relative standard deviation (RSD) of at least 3 measurements.

2.3 Quantification of O_3 Initial Concentration:

The initial O_3 concentration of the saturated O_3 solution was measured with a UV-Vis spectrophotometer at λ = 260nm in a quartz cuvette (λ = 1 cm). By using the extinction co-efficient of O_3 (ε_{260} =2900 $cm^{-1} \cdot M^{-1}$) the molarity of the saturated solution was estimated. Specific volumes of the solution were added in each batch bottle to give a theoretical O_3 concentration. The actual O_3 concentration was quantified with the Indigo method [34, 40].

2.4 Quantification of Initial Oxidant Concentration:

The initial concentration of ClO^-, ClO_2 and CH_3COOO^- was measured photometrically with the HACH LANGE DR2800. ClO^- was measured in the "free chlorine mode" by adding 3 drops of phosphate buffer (pH = 2.0), 1 drop of N,N-diethyl-p-phenylenediamine, DPD (5 g/L) and 10 mL of ClO^- solution (5 mL from concentrated stock in 1000mL of Milli-Q water). ClO_2 was measured in the "ClO_2 mode" by following the same procedure as ClO^-. Finally, CH_3COOO^- was measured in the Cl_2 mode by adding 3 drops of potassium iodide (5 g/L) 1 drop of DPD (5 g/L) and 10 mL of dilute CH_3COOO^- solution.

2.5 HPLC Analysis:

Atrazine (FW = 215.69) was quantified with an Agilent 1100 Series HPLC equipped with a variable wavelength detector (VWD). A C_{18} column (46 mm x 15 cm, 5 μm particle size) from Supelco Discovery was utilized. The eluent phase was 50:50 acetonitrile:H_2O, with a flow rate of 0.5 mL/min, T_{column} = 25.5°C and the detector set at λ = 220 nm. Based on these conditions atrazine eluted at RT = 8.2 min. Calibration curves with standard solutions at 10– 1000 μg/L were conducted and the method quantification limit was set at 5 μg/L.

2.6 Ion Chromatography Analysis:

Determination of BrO_3^- concentration was performed via ion chromatography coupled with a post column reaction with KI that resulted in the formation of I_3^- which was measured in a UV detector (based on the method of Salhi *et al.*, 1999 [41]. More information on the IC analysis can be retrieved from Antoniou and Andersen (2012) [34].

3. Results and Discussion

3.1 Effect of pre-treatment type and added concentrations:

The aim of this study was to find appropriate pre-treatments based on the "Cl_2/NH_4^+" pre-treatment so that the formation of carcinogenic BrO_3^- during ground-water ozonation is limited below 10.0 μg/L and to evaluate how much these pre-treatments affect atrazine removal. The applied concentrations of NH_4^+ and oxidant (Cl_2) concentrations were within the range of literature reports [30, 31]. NH_4^+ was added at 1.0 mg/L, which has a molar ratio to Br^- equal to $[NH_4^+]/[Br^-]$ = 44. The oxidants used, were added in the same molar concentrations as

Cl_2 starting at 1.0 mg/L equivalent Cl_2, which is equal to 15.0 μM and gives a molar ratio to bromide [Ox]/[Br^-] = 12. The doses for both NH_4^+ and Cl_2 were doubled and quadrupled to account for the added concentration effects. Overall, the oxidants HSO_5^- $S_2O_8^{-2}$, ClO_2, ClO_2^-, ClO^-, CH_3COOO^- and MnO_4^- were tested under the abovementioned conditions. Initially, control experiments with 3.5 mg/L O_3 (as determined by the indigo method) were conducted in the batch reactors to account for the amount of BrO_3^- formed during treatment. Next, NH_4^+ was added at molar concentrations equal to [NH_4^+]/[Br^-] = 44, 88, 178 and allowed 15 min of reaction, and then 3.5 mg/L O_3 were added and left to react overnight in a 15°C water bath. For the experiments with the oxidants, the oxidant was added first, allowed 15min of reaction time, then NH_4^+ was added and allowed another 15 min of reaction time before adding 3.5 mg/L O_3. The formation of BrO_3^- and reduction of the ATR's concentration were determined for all the experiments.

Figure 1 summarizes the results from the different pre-treatments on the BrO_3^- formation (left axis) and remaining atrazine (right axis). Ozonation of DTU tap water with 3.5 mg/L O_3, resulted in the formation of 160.0±19.0 BrO_3^- μg/L. Based on the fact that the initial Br^- concentration was 100 μg/L, 3.5 mg/L O_3 has completely transformed Br^- to BrO_3^-. Addition of excess NH_4^+ (which reacts with $HOBr/OBr^-$ to form NH_2Br), decreased BrO_3^- formation ~75% compared to the O_3 control, irrespective of the NH_4^+ dosing. This means that lower concentrations than 1.0 mg/L NH_4^+ ([NH_4^+]/[Br^-] = 44) could be efficiently used in DTU-water as they have been reported for lake water [30, 42]. It was expected that ammonia alone would not be able to completely control bromate below the 10 μg/L limit since it does not influence bromate formation with the radical pathway during the initial phase of ozonation [30]. As expected, Cl_2/NH_4^+ (as ClO^-) greatly inhibited BrO_3^- formation compared to O_3 alone. With increasing oxidant and NH_4^+ concentrations, bromate formation reduced from 20 μg/L to below the method detection limit (BDL). ClO_2/NH_4^+, ClO_2^-/NH_4^+ and MnO_4^-/NH_4^+ were the most efficient pre-treatments, since bromate formation was BDL for all oxidant concentrations (except for 15.0 μM MnO_4^- which was on the limit). Besides BrO_3^-, these oxidants can oxidize the active sites of NOM [18, 43] which is found in higher concentrations compared to the other matrix components (2.5 mg/L DOC). Given that NOM is known to accelerate O_3 decomposition [18], this has a direct impact on O_3 exposure (C·t), which becomes shorter, and results in decreased BrO_3^- formation. In addition, NOM competes with the contaminant for oxidation by the active species, therefore reducing the level of contaminant degradation. Since these oxidants were equally efficient for all the range of concentrations, it is implied that lower concentrations can be used and still control BrO_3^- formation below the set drinking water limit. The oxidants HSO_5^- and $S_2O_8^{-2}$ that follow free radical mechanisms ($SO_4^{\bullet-}$ and $HO^{\bullet}$) for oxidation [44, 45], did not perform as well as expected with NH_4^+, especially HSO_5^- which performed worse than NH_4^+ alone. One possible explanation could be that the reaction time was not sufficient for the oxidants to effectively oxidize Br^- to OBr^-, but longer reaction times would be technically impractical. Since the inhibition of BrO_3^- formation, relies on the efficiency of the oxidant to convert Br^- to OBr^- prior to ozonation, it is apparent that HSO_5^- and $S_2O_8^{-2}$ necessitate either additional reaction time or further catalytic activation to convert them into oxidizing radical species [44, 45]. The increase of BrO_3^- concentration with HSO_5^-/NH_4^+ could be attributed to $HO^{\bullet}$ formed during its decomposition that enhance the radical based oxidation route of Br^-. CH_3COOO^- had the same efficiency on BrO_3^- formation as NH_4^+, which means that it did not cause notable oxidation of Br^-. Overall, the effectiveness on inhibiting BrO_3^- formation followed the order of: $KMnO_4/NH_4^+ = ClO_2/NH_4^+ = ClO_2^-/NH_4^+ > NaClO/NH_4^+ > NH_4^+ > CH_3COOO^-/NH_4^+ > S_2O_8^{-2}/NH_4^+ > HSO_5^-/NH_4^+$.

The right axis of Figure 1, depicts the remaining atrazine concentration following the different pre-treatments and ozonation. Based on our previous studies [34], an O_3 concentration of 3.5 mg/L was adequate to remove atrazine (90.3% ± 3.0%) and was used as the O_3 delivered concentration throughout this study. The presence of NH_4^+ reduced atrazine removal to 78.0 ± 8.0%. This may be attributed to the consumption of O_3 by reacting with NH_4^+ instead (as NH_3, $k_{O3,NH3}$= 20.0±2.0 $M^{-1}s^{-1}$ [46], $k_{OH,NH3}$= 1.0± 0.1·10^8 $M^{-1}s^{-1}$ [47]. Though at pH =7.0 only 0.22-0.88 μmol/L of ammonia are present as $NH_{3(aq)}$ (pka_{NH4+} = 9.3, [NH_4^+]$_o$= 5.5-22.0 μmol/L), since atrazine concentration is 0.09 μmol/L ($k_{ATR,O3}$ = 6.0-6.3 $M^{-1}s^{-1}$ & $k_{ATR,HO}$ = 2.5-3.0·10^9 $M^{-1}s^{-1}$) [38], $NH_{3(aq)}$ becomes a

significant competitor for both O_3 and $HO^{\bullet}$ degradation. The effect of the presence of NH_4^+ on atrazine removal is noticeable because the latter is primarily removed through reaction with $HO^{\bullet}$ formed through O_3 decomposition.

NH_4^+ was not the only pre-treatment that inhibited atrazine removal. In fact, HSO_5^-/NH_4^+ and $S_2O_8^{-2}/NH_4^+$ and CH_3COOO^-/NH_4^+ inhibited atrazine removal in the same range as NH_4^+. It is believed that these oxidants under our experimental conditions were not sufficiently activated to form the radical that can oxidize bromide to bromate and therefore, the effect on atrazine removal is mainly attributed to the presence of NH_4^+. Pre-treatments with ClO_2^-/NH_4^+, ClO_2/NH_4^+ and ClO^-/NH_4^+ affected atrazine removal the most, with the efficiencies varying between 35.0-75.0% for the different oxidant concentrations. MnO_4^-/NH_4^+, besides controlling BrO_3^- formation at the 10 μg/L limit did not influence atrazine removal (90.0±1.0%) for all the oxidant concentrations. The reproducibility of the experiments was tested in a separate experiment summarized in the supplementary information document (S.I., Figure S1).

3.2 Pre-treatment with ClO_2, ClO_2^- and MnO_4^-: Effect of oxidant and NH_4^+ concentration and addition stages:

With ClO_2/NH_4^+ and ClO_2^-/NH_4^+ and MnO_4^-/NH_4^+ exhibiting the highest potential for preventing BrO_3^- formation during ozonation, these oxidants were further investigated. Figure 1, indicates that lower oxidant and NH_4^+ concentrations could potentially be used, while reaching the treatment goals. Therefore, the oxidant concentrations were reduced to doses between 1.5 and 15 μM ([Ox]/[Br^-]= 1.2-12.0), while NH_4^+ was kept at 1.0 mg/L ([NH_4^+]/[Br^-] = 44). Based on the results shown in Figure 2A, for ClO_2/NH_4^+ and ClO_2^-/NH_4^+, BrO_3^- formation was approximately 22.0 μg/L for all concentrations except for 0.1 mg/L ClO_2^- (C=1.5 μM) which gave 30 ± 7 μg/L BrO_3^-. For these two oxidants, BrO_3^- formation was better controlled when the higher range of oxidant and NH_4^+ concentrations were used (Figure 1). In the case of MnO_4^-/NH_4^+, only at 2.4 MnO_4^- mg/L BrO_3^- formation was below the 10.0 μg/L limit while for the remaining concentrations it was ~18μg/L. On the other hand, with reduced oxidant concentrations and 1.0 mg/L NH_4^+, atrazine removal greatly improved for ClO_2/NH_4^+ and ClO_2^-/NH_4^+. For ClO_2^- it was 85.0% for all oxidant concentrations, while for ClO_2, atrazine removal reduced with increasing oxidant concentration from 85% to 75%. As far as MnO_4^-/NH_4^+, the efficiency reached almost 90% for all oxidant concentrations (Figure 2A). When it comes to atrazine removal, the effect of ClO_2 and ClO_2^- with O_3 is not additive since they are exerting an ozone demand (as explained in Section 3.4). Also, when used alone O_3 and MnO_4^- react very slowly with atrazine (k_{O3} = 6.0-6.3 $M^{-1}s^{-1}$ [38]; k_{MnO4^-} = 1.16 $M^{-1}s^{-1}$ [48]), while ClO_2 and ClO_2^- have been reported not to react [49]. Based on our results, O_3 and MnO_4^- can co-exist without inhibiting each other's oxidative action on atrazine and Br^-, respectively. On the contrary, ClO_2 and ClO_2^- greatly affect the oxidation capacity of O_3. One possible reason (explained in greater detail later on and in Figure 4) could be the preferential reaction of ClO_2^- with O_3 to form ClO_2 which limits O_3 exposure and thus $HO^{\bullet}$ production. When ClO_2 and ClO_2^- are reduced, the loss of O_3 is also reduced and more O_3 (and therefore $HO^{\bullet}$) are available for atrazine removal. Based on this experiment, it was decided to use 0.6 mg/L ClO_2, 0.6 mg/L ClO_2^- and 1.4 and 2.4 mg/L MnO_4^- as the optimum oxidant concentrations for the remaining experiments.

Since the effect of reduced oxidant concentration was beneficial towards the treatment goals, the effect of reduced NH_4^+ concentration was tested next at, the previously determined, reduced oxidant concentrations. The new NH_4^+ concentration was 0.1 and 0.4 mg/L (equal to [NH_4^+]/[Br^-] = 4.4; 17.6). Even though, the added NH_4^+ is significantly less, it is still in excess compared to Br^-, and should be sufficient for the reaction of BrO^- to NH_2Br. Based on the results depicted in Figure 2B, for the ClO_2/NH_4^+ pre-treatment, NH_4^+ reduction to 0.1 mg/L reduced BrO_3^- formation to 10.0 μg/L, while at the same time atrazine removal was 87.0%. For 0.4 mg/L NH_4^+, the efficiency for BrO_3^- formation was BDL and atrazine removal 82.0%. For ClO_2^-/NH_4^+, BrO_3^- formation increased to 40 μg/L at 0.1 mg/L NH_4^+ and decreased BDL for 0.4 NH_4^+ mg/L, while atrazine removal was at 90.0% with 0.1 mg/L NH_4^+, and decreased to 85% when 0.4 mg/L NH_4^+ were used. For MnO_4^-/NH_4^+, 1.4 and 2.4 mg MnO_4^- /L were used with the low NH_4^+ concentrations since they had similar efficiencies (Figure 2A). From the results depicted in Figure 2B, it is determined that 0.4 mg/L of NH_4^+ are needed for MnO_4^- to be effective in controlling BrO_3^- formation. Also, 1.4 mg/L of MnO_4^- was not sufficient to oxidize Br^- to OBr^-, and therefore, at

least 2.4 mg MnO_4^-/L should be used. Atrazine removal maintained around 87.0% irrespective of the experimental conditions.

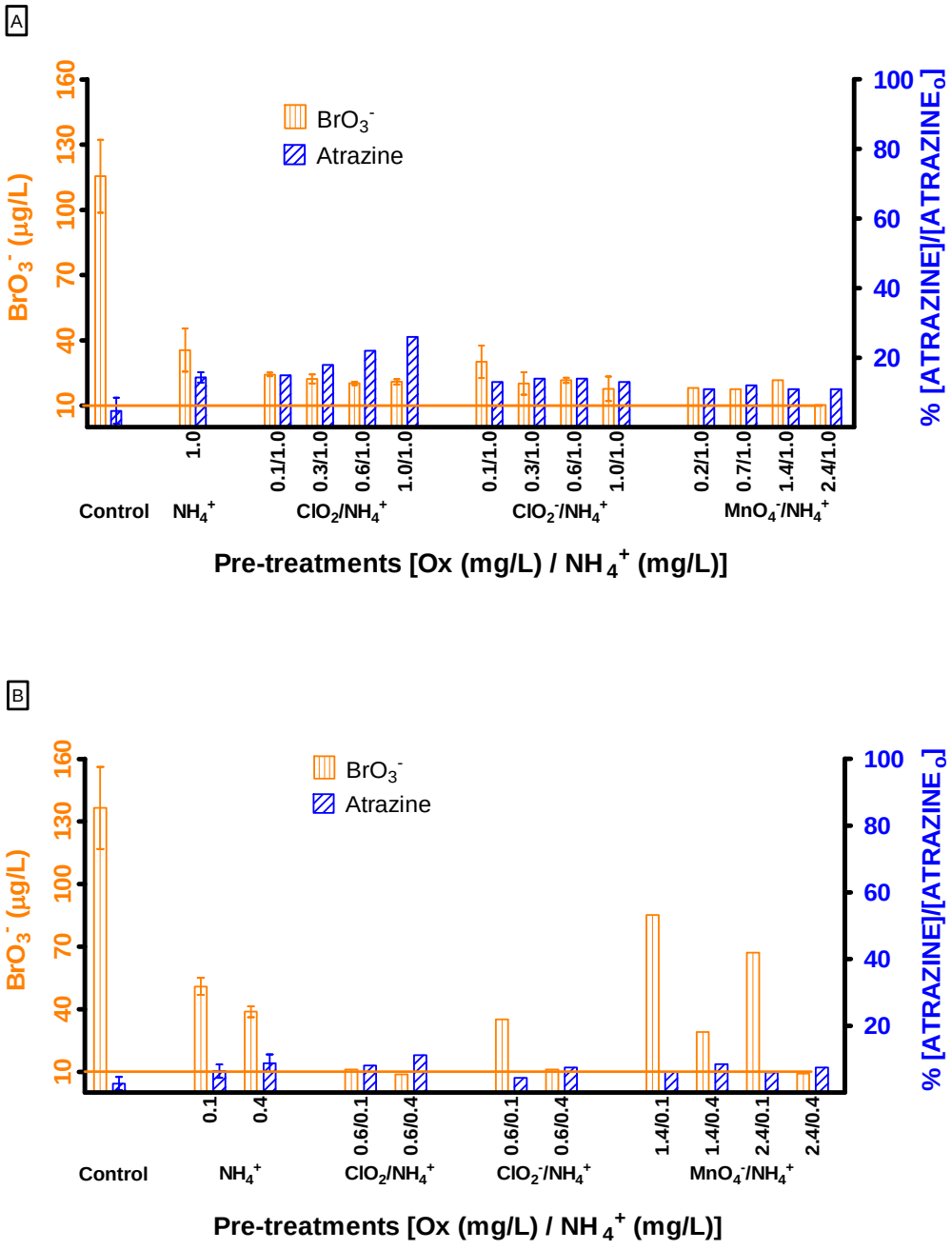

Figure 2A: Effect of reduced oxidant doses (ClO_2 and ClO_2^- and MnO_4^-) on BrO_3^- formation and remaining atrazine concentration. Experimental conditions: O_3= 3.5 mg/L; Br^- = 100 µg/L; ATR_o= 200 µg/L; NH_4^+ = 1.0 mg/L; $[NH_4^+]/[Br^-]$ = 44.0; [Ox] =1.5, 4.5, 9.0,15.0 µM; $[Ox]/[Br^-]$ = 1.2, 3.6, 7.2, 12.0.; pH= 7.0. 2B: Effect of reduced ammonia doses on BrO_3^- formation and remaining atrazine concentration for ClO_2 and ClO_2^- at $[Ox]/[Br^-]$= 7.2 and MnO_4^- at $[Ox]/[Br^-]$= 7.2, 12.0. Experimental conditions: O_3= 3.5 mg/L; Br^- = 100 µg/L; ATR_o= 200 µg/L; NH_4^+= 0.1, 0.44 mg/L; $[NH_4^+]/[Br^-]$ = 4.4, 17.6; [Ox] =9.0,15.0 µM; $[Ox]/[Br^-]$ = 7.2, 12; pH= 7.0.

To summarize, the optimum concentrations to reach the treatment goals are 0.6 mg/L ClO_2 ($[Ox]/[Br^-]$= 7.2) with 0.1 mg/L NH_4^+ ($[NH_4^+]/[Br^-]$ = 4.4); 0.6 mg/L ClO_2^- ($[Ox]/[Br^-]$= 7.2) with 0.4 mg/L NH_4^+ ($[NH_4^+]/[Br^-]$ = 4.4) and 2.4 mg/L MnO_4^- ($[Ox]/[Br^-]$= 7.2) with 0.4 mg/L NH_4^+ ($[NH_4^+]/[Br^-]$ = 4.4).

Simultaneous (single stage) addition of the oxidant and NH_4^+ is technically more advantageous than two stage addition because it reduces treatment time and thus tank size in the waterworks. To test whether the effectiveness of ClO_2, ClO_2^- and MnO_4^- with NH_4^+ to inhibit BrO_3^- formation is affected by the addition stages, experiments with [Ox]/[Br^-]= 7.2 and 1.0 mg/L NH_4^+ were performed. The results on BrO_3^- formation and atrazine removal (Figure 3) do not vary statistically (t-testing, 95% confidence) and therefore, pre-treatments with these oxidants, in contrast to Cl_2/NH_4^+, are proven not to be dependent on the addition stages.

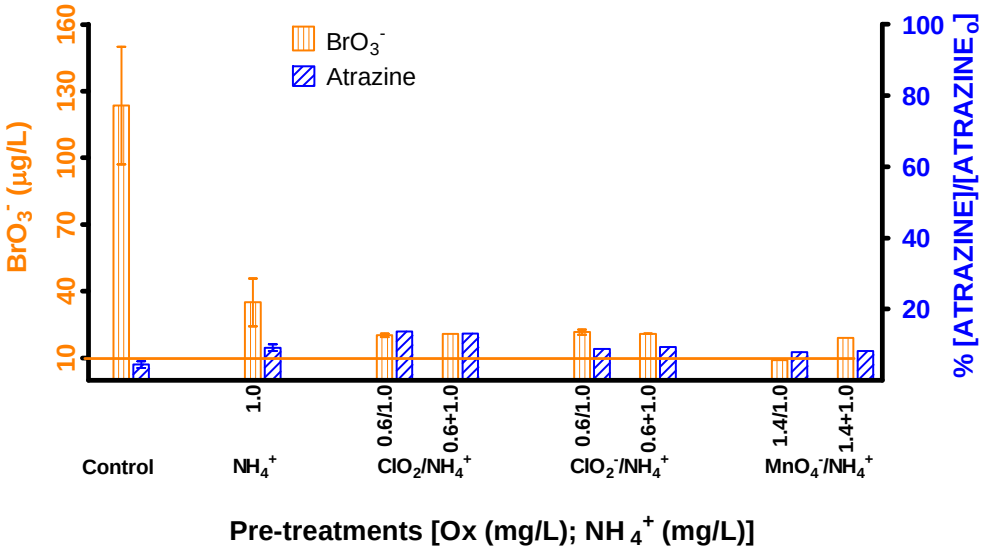

Figure 3: Effect of oxidants (ClO_2 and ClO_2^- and MnO_4^-) and NH_4^+ addition for single (Ox +NH_4^+, t =30 min) and two stage addition (Ox /NH_4^+, t=15+15 min). Experimental conditions: O_3= 3.5 mg/L; Br^- = 100 µg/L; ATR_o= 200 µg/L; NH_4^+ = 1.0 mg/L; [NH_4^+]/[Br^-] = 44; [Ox] =9.0 µM; [Ox]/[Br^-] = 7.2; pH= 7.0.

3.3 Pre-treatment with ClO_2, ClO_2^-, and MnO_4^- in the absence of NH_4^+:

In an effort to unveil the mechanisms that inhibit BrO_3^- formation with ClO_2, ClO_2^-, and MnO_4^-, experiments in the absence of NH_4^+ were conducted. Concentrations of 0.6 mg/L were used for ClO_2, ClO_2^-, ([Ox]/[Br^-]= 7.2) and 2.4 mg/L MnO_4^- ([Ox]/[Br^-]= 12). Each oxidant was left to react for 15 min prior to the addition of 3.5 mg/L O_3. It is apparent from Figure 4 that the absence of NH_4^+ resulted in a drastic increase of BrO_3^- formation for all the oxidants (compared to Figure 2B) and especially for 2.4 mg/L MnO_4^-, that yielded the same BrO_3^- concentration as the O_3 control.

There are two more studies in the literature in which addition of permanganate in the absence of ammonia was investigated as a pre-treatment to ozonation [50-51]. Dong *et al.* (2010) reported that addition of 1.0 mg/L $KMnO_4$ could decrease BrO_3^- formation by 26 % in water containing 100 µg/L bromide, 5 mg/L humic acids, for an added O_3 dose of 5.6 mg/L and reaction time of 30 min. In the absence of humic acid an approximate 20% reduction of BrO_3^- formation was reported in similar reaction conditions [50]. Liu *et al.* (2014) also reported that $KMnO_4$ alone can inhibit BrO_3^- formation for 0.4 mg/L O_3 without providing further explanation on their findings [51]. These results differ from the findings of our study, where absolutely no inhibition of bromate formation by permanganate was achieved without the co-addition of ammonia. This may be explained by the differences in the experimental conditions between studies (water matrix, O_3 dose). Dong *et al.* (2010) hypothesized that the observed decrease in bromate formation is caused by catalytic and reductive consumption of ozone by manganese oxides formed from MnO_4^- which compete with bromide for ozone. This suggested mechanism implies that removal of target chemicals for the ozone treatment, like atrazine in our study, would decrease by permanganate addition, but inhibition of atrazine removal was not observed in this study in the presence or absence of ammonia.

Addition of ClO_2 and ClO_2^- yielded 50.0 µg/L and 42.0 µg/L of BrO_3^-, respectively. The results (Figure 4) confirmed the importance of NH_4^+ for the pre-treatments to be effective in preventing BrO_3^- formation. In the absence of NH_4^+, the *in situ* generated OBr^- (from the oxidation of ClO_2, ClO_2^-, and MnO_4^-) exclusively

transforms to BrO_3^- with ozonation. Atrazine removal was less affected by the absence of NH_4^+ and was ~85.0% for ClO_2 and ClO_2^- and 95.0% for MnO_4^-.

Figures

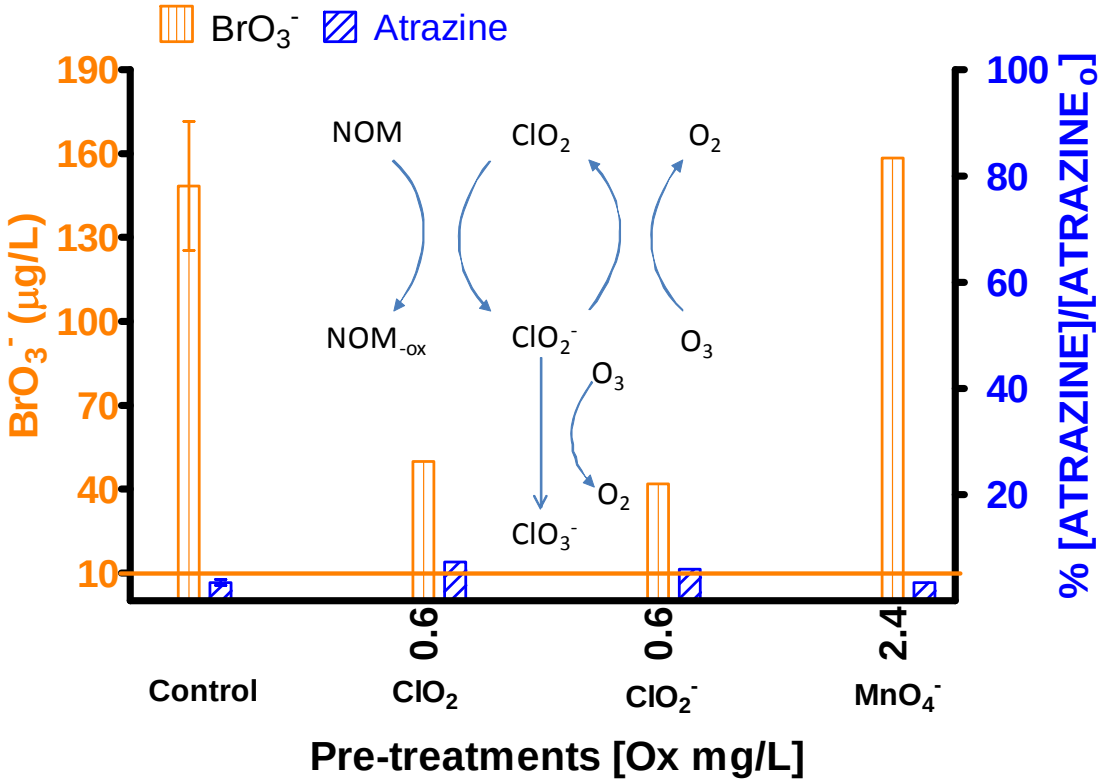

Figure 4: Pre-treatment with ClO_2, ClO_2^-, and MnO_4^- in the absence of NH_4^+ following ozonation. Experimental conditions: O_3= 3.5 mg/L; Br^- = 100 µg/L; ATR_o= 200 µg/L; [Ox] =9.0 µM; [Ox]/[Br^-] = 7.2. For 2.4 mg/L MnO_4^-, [Ox] =15 µM; [Ox]/[Br^-] = 12; pH= 7.0.

3.4 Proposed secondary mechanisms for ClO_2 and ClO_2^- inhibition of BrO_3^- formation:

Based on the findings of this study, side mechanisms that inhibit BrO_3^- formation are proposed (Figure 4). The main mechanism behind the inhibition of BrO_3^- formation in the pre-treatments ClO_2, ClO_2^-, and MnO_4^- with NH_4^+ is:

Oxidant $+Br^- \rightarrow BrO^-$; $BrO^- + NH_4^+ \rightarrow NH_2Br$ (Eq.1) [8, 30, 31]

However, the experiment with ClO_2, ClO_2^-, and MnO_4^- in the absence of NH_4^+ indicated the existence of another mechanism that affects BrO_3^- formation and atrazine removal (Figure 4). Prior to ozonation, ClO_2 reacts with NOM and becomes ClO_2^-. The NOM in DTU-tap water reduces 0.6 mg/L ClO_2 to ClO_2^- almost instantaneously (unpublished data). Once the solution is ozonated, the added or *in situ* formed (from ClO_2) ClO_2^-, rapidly reacts with O_3 and produces ClO_3^- (terminal reaction) or regenerates ClO_2 (cyclic reaction). These reactions reduce the available O_3 for oxidation of brominated species and therefore less BrO_3^- is formed. This is the reason why in the absence of NH_4^+ with ClO_2 and ClO_2^-, BrO_3^- formation is 31.0% and 26.0% of the O_3 control, respectively. This experiment indicates that MnO_4^- did not follow a similar mechanism and therefore, BrO_3^- formation with MnO_4^- pre-treatment in the absence of NH_4^+ was the same as the O_3 control.

It was also observed, that pre-treatment with ClO_2/NH_4^+ required 0.1 mg/L of NH_4^+ to inhibit BrO_3^- formation while ClO_2^- required 0.4 mg/L of NH_4^+, at the same molar concentration. This is likely due to the fact that ClO_2 is a stronger oxidant that ClO_2^- and it is able to oxidize Br^- to HOBr/OBr^-, prior to ozonation. ClO_2^- can only initiate

Br^- oxidation when it is oxidized by O_3 to ClO_2 (Figure 4). Therefore, excess NH_4^+ is required to insure conversion of $HOBr/OBr^-$ to NH_2Br (since this reaction is in competition with the others that lead to the further oxidation of $HOBr/OBr^-$ to BrO_2^- and BrO_3^-).

3.5 Estimated cost of pretreatments:

With the focus of this study placed on the feasibility of various pretreatments for BrO_3^- control during ozonation, the additional chemical cost at the optimum conditions of each pre-treatment was calculated, based on market prices (Germany, collected in August 2010) for bulk chemicals as given by relevant suppliers (Supplementary information, Table S1). Thus, the running cost for chemicals for the pretreatment with ClO_2/NH_4^+, ClO_2^-/NH_4^+, and MnO_4^-/NH_4^+, were estimated at 2.1, 0.8, and 3.8 c€/m^3, respectively. This is a reasonable price compared to the total costs of drinking water production.

So far, we are aware of two treatment facilities in Netherlands (PWN Water Supply Company and DUNEA) that are treating similar type of water matrixes to DTU tap water for ECs removal (including atrazine) and have naturally high content of Br^- (300-500 μg/L). PWN decided to install a UVC/H_2O_2 treatment instead of O_3 ([23], while DUNEA used a multiple barrier approach of combined O_3/H_2O_2 and UVC (at low UV and O_3 doses) [52]. It is our belief that the proposed new pre-treatment could allow more economical solutions for such cases in the future. Based on the treatment goals that each facility has, they may choose the MnO_4^-/NH_4^+ pre-treatment was the most efficient for achieving a log removal of atrazine and inhibiting bromate formation below 10 µg/L, or the less expensive ClO_2^-/NH_4^+, if the requirements for atrazine removal are reduced to 70%.

4. Conclusions

To conclude, among the array of oxidants tested, ClO_2, ClO_2^-, and MnO_4^- with NH_4^+ were the most promising pre-treatments for controlling BrO_3^- formation and atrazine removal during the ozonation of ground-water. By varying the oxidant and NH_4^+ concentrations, the optimum conditions of each of the abovementioned pre-treatments were determined to be: 0.6 mg/L ClO_2/0.1 mg/L NH_4^+, 0.6 mg/L ClO_2^- / 0.4 mg/L NH_4^+, and 2.4 mg/L MnO_4^-/0.4 mg/L NH_4^+. These pre-treatments were found not to be affected by the addition steps (single or two stage addition). Experiments performed in the absence of NH_4^+, confirmed its importance on the mechanism that reduces BrO_3^- formation during ozonation, as well as side mechanisms that affect BrO_3^- formation and atrazine removal. Finally, the running cost for chemicals for the pretreatment with ClO_2/NH_4^+, ClO_2^-/NH_4^+, and MnO_4^-/NH_4^+, were estimated at 2.1, 0.8, and 3.8 c€/m^3, respectively which is considered reasonable for drinking water production.

Acknowledgments

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Supplementary information

Supplementary data associated with this article can be found in a separate document.

References:

[1] A.A. de la Cruz, M.G. Antoniou, A. Hiskia, M. Pelaez, W. Song, K.E. O'Shea, X. He, D.D. Dionysiou, Can we effectively degrade microcystins? - implications on human health, Anti-Cancer Agents in Medicinal Chemistry. 11 (2011) 19-37.

[2] J. Hollender, S.G. Zimmermann, S. Koepke, M. Krauss, C.S. Mcardell, C. Ort, H. Singer, U. Von Gunten, H. Siegrist, Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a

full-scale post-ozonation followed by sand filtration, Environmental Science and Technology. 43 (2009) 7862-7869.

[3] G.D. Onstad, S. Strauch, J. Meriluoto, G.A. Codd, U. Von Gunten, Selective oxidation of key functional groups in cyanotoxins during drinking water ozonation, Environmental Science and Technology. 41 (2007) 4397-4404.

[4] M.M. Huber, S. Canonica, G.-. Park, U. Von Gunten, Oxidation of pharmaceuticals during ozonation and advanced oxidation processes, Environmental Science and Technology. 37 (2003) 1016-1024.

[5] M. Esperanza, M.T. Suidan, R. Marfil-Vega, C. Gonzalez, G.A. Sorial, P. McCauley, R. Brenner, Fate of sex hormones in two pilot-scale municipal wastewater treatment plants: Conventional treatment, Chemosphere. 66 (2007) 1535-1544.

[6] B.L. Loeb, Ozone: Science and engineering: Thirty-three years and growing, Ozone: Science and Engineering. 33 (2011) 329-342.

[7] M.M. Huber, A. Göbel, A. Joss, N. Hermann, D. Löffler, C.S. McArdell, A. Ried, H. Siegrist, T.A. Ternes, U. Von Gunten, Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: A pilot study, Environmental Science and Technology. 39 (2005) 4290-4299.

[8] U. Von Gunten, Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine, Water Res. 37 (2003) 1469-1487.

[9] S. Chiron, A. Fernandez-Alba, A. Rodriguez, E. Garcia-Calvo, Pesticide chemical oxidation: State-of-the-art, Water Res. 34 (2000) 366-377.

[10] K. Lekkerkerker, J. Scheideler, S.K. Maeng, A. Ried, J.Q.J.C. Verberk, A.H. Knol, G. Amy, J.C. Van Dijk, Advanced oxidation and artificial recharge: A synergistic hybrid system for removal of organic micropollutants, Water Science and Technology: Water Supply. 9 (2009) 643-651.

[11] K.M.S. Hansen, H.R. Andersen, A. Ledin, Ozonation of estrogenic chemicals in biologically treated sewage, Water Science and Technology. 62 (2010) 649-657.

[12] M.G. Antoniou, G. Hey, S. Rodríguez Vega, A. Spiliotopoulou, J. Fick, M. Tysklind, J. la Cour Jansen, H.R. Andersen, Required ozone doses for removing pharmaceuticals from wastewater effluents, Sci. Total Environ. 456-457 (2013) 42-49.

[13] J. Tuerk, B. Sayder, A. Boergers, H. Vitz, T.K. Kiffmeyer, S. Kabasci, Efficiency, costs and benefits of AOPs for removal of pharmaceuticals from the water cycle, Water Science and Technology. 61 (2010) 985-993.

[14] H. Kusic, N. Koprivanac, A.L. Bozic, Minimization of organic pollutant content in aqueous solution by means of AOPs: UV- and ozone-based technologies, Chem. Eng. J. 123 (2006) 127-137.

[15] M.J. Watts, K.G. Linden, Chlorine photolysis and subsequent OH radical production during UV treatment of chlorinated water, Water Res. 41 (2007) 2871-2878.

[16] C. Sichel, C. Garcia, K. Andre, Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants, Water Res. 45 (2011) 6371-6380.

[17] A. Driedger, E. Staub, U. Pinkernell, B. Mariñas, W. Köster, U.v. Gunten, Inactivation of bacillus subtilis spores and formation of bromate during ozonation, Water Res. 35 (2001) 2950-2960.

[18] U. von Gunten, The basics of oxidants in water treatment. Part B: Ozone reactions, Water Science and Technology. 55 (2007) 25-29.

[19] K.L. Rakness, Ozone in Drinking Water Treatment: Process Design, Operation and Optimization (2005) American Water Work Association, Denver, USA, pp 302.

[20] J. Staehelln, J. Hoigné, Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide, Environmental Science and Technology. 16 (1982) 676-681.

[21] S.G. Zimmermann, M. Wittenwiler, J. Hollender, M. Krauss, C. Ort, H. Siegrist, U. von Gunten, Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection, Water Res. 45 (2011) 605-617.

[22] B. Legube, B. Parinet, F. Berne, J.-. Croue, Bromate surveys in French drinking waterworks, Ozone: Science and Engineering. 24 (2002) 293-304.

[23] J.C. Kruithof, P.C. Kamp, B.J. Martijn, UV/H2O2 treatment: A practical solution for organic contaminant control and primary disinfection, Ozone: Science and Engineering. 29 (2007) 273-280.

[24] Y. Kurokawa, A. Maekawa, M. Takahashi, Y. Hayashi, Toxicity and carcinogenicity of potassium bromate - A new renal carcinogen, Environ. Health Perspect. 87 (1990) 309-335.

[25] Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption (1998).

[26] USEPA 2010. Unites States Environmental Protection Agency (US EPA) Revised State Implementation Guidance for the Consumer Confidence Report (CCR) Rule.

[27] S. Liang, T.I. Yun, S.W. Krasner, R.S. Yates, Evaluation of Emerging Bromate Control Strategies, American Water Works Association Annual Conference and Exposition 2012, ACE 2012 (2010) 1-10.

[28] M.D. Williams, B.M. Coffey, S.W. Krasner, Evaluation of pH and ammonia for controlling bromate during Cryptosporidium disinfection, J. Am. Water Works Assoc. 95 (2003) 82-93.

[29] USEPA 2006. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule EPA-HQ-OW-2002-0043. Publication date 4th January, 2006

[30] U. Pinkernell, U. Von Gunten, Bromate minimization during ozonation: Mechanistic considerations, Environmental Science and Technology. 35 (2001) 2525-2531.

[31] M. Buffle, S. Galli, U. Von Gunten, Enhanced bromate control during ozonation: The chlorine-ammonia process, Environmental Science and Technology. 38 (2004) 5187-5195.

[32] D.D. Rittmann, Impact of chlorine dioxide pre-oxidation of ozone on bromate formation, Am. Water Works Assoc. - Water Qual. Technol. Conf. Expo. : Taking Water Qual. New Heights (2006) 648-666.

[33] F. Parrino, G. Camera-Roda, V. Loddo, V. Augugliaro, L. Palmisano, Photocatalytic ozonation: Maximization of the reaction rate and control of undesired by-products, Applied Catalysis B: Environmental. 178 (2015) 37-43.

[34] M.G. Antoniou, H.R. Andersen, Evaluation of pretreatments for inhibiting bromate formation during ozonation, Environmental Technology (United Kingdom). 33 (2012) 1747-1753.

[35] R. Song, P. Westerhoff, R. Minear, G. Amy, Bromate minimization during ozonation, Journal American Water Works Association. 89 (1997) 69-75.

[36] D. Eberle, Z. Chowdhury, L. Passantino, S. Bontrager, Mitigation of ozone-induced bromate by carbon dioxide and chlorine/ammonia processes, Environmental Engineer: Applied Research and Practice. 7 (2009) 29-38.

[37] F.J. Beltrán, J.F. García-Araya, P.M. Álvarez, J. Rivas, Aqueous degradation of atrazine and some of its main by-products with ozone-hydrogen peroxide, Journal of Chemical Technology and Biotechnology. 71 (1998) 345-355.

[38] J.L. Acero, K. Stemmler, U. Von Gunten, Degradation kinetics of atrazine and its degradation products with ozone and OH radicals: A predictive tool for drinking water treatment, Environmental Science & Technology 2000. 34 (2000) 591-597.

[39] WFD 2000, Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32000L0060 (last accessed: March 3rd, 2016)

[40] H. Bader, J. Hoigne, Determination of ozone in water by the indigo method, Water Res. 15 (1981) 449-456.

[41] E. Salhi, U. Von Gunten, Simultaneous determination of bromide, bromate and nitrite in low µg l-1 levels by ion chromatography without sample pretreatment, Water Res. 33 (1999) 3239-3244.

[42] W.R. Haag, J. Hoigné, H. Bader, Improved ammonia oxidation by ozone in the presence of bromide ion during water treatment, Water Res. 18 (1984) 1125-1128.

[43] M. Buffle, J. Schumacher, S. Meylan, M. Jekel, U. Von Gunten, Ozonation and advanced oxidation of wastewater: Effect of O3 dose, pH, DOM and HO.-scavengers on ozone decomposition and HO . generation, Ozone: Science and Engineering. 28 (2006) 247-259.

[44] M.G. Antoniou, A.A. De La Cruz, D.D. Dionysiou, Intermediates and reaction pathways from the degradation of microcystin-LR with sulfate radicals, Environmental Science and Technology. 44 (2010) 7238-7244.

[45] M.G. Antoniou, A.A. de la Cruz, D.D. Dionysiou, Degradation of microcystin-LR using sulfate radicals generated through photolysis, thermolysis and e- transfer mechanisms, Applied Catalysis B: Environmental. 96 (2010) 290-298.

[46] H. Hoigne, H. Bader, Rate constants of reactions of ozone with organic and inorganic compounds in water. II. Dissociating organic compounds, Water Res. 17 (1983) 185-194.

[47] L. Huang, L. Li, W. Dong, Y. Liu, H. Hou, Removal of ammonia by OH radical in aqueous phase, Environmental Science and Technology. 42 (2008) 8070-8075.

[48] S.N. Gibson, Oxidation of pharmaceuticals and personal care products by permanganate. , Georgia Institute of Technology, Atlanta, (2010) 1-92.

[49] B.W. Lykins Jr., W. Koffskey, Products identified at an alternative disinfection pilot plant, Environ. Health Perspect. Vol. 69 (1986) 119-128.

[50] W. Dong, Z. Dong, F. Ouyang, Y. Dong, Potassium permanganate/ozone combined oxidation for minimizing bromate in drinking water, Advanced Materials Research. 113-116 (2010) 1490-1495.

[51] Z. Liu, Y. Cui, J. Chen, Z. Yan, The control of bromate formation in ozonation of bromide-containing water, Desalin. Water Treat. 52 (2014) 4942-4946.

[52] K. Lekkerkerker-Teunissen, A.H. Knol, L.P. Van Altena, C.J. Houtman, J.Q.J.C. Verberk, J.C. Van Dijk, Serial ozone/peroxide/low pressure UV treatment for synergistic and effective organic micropollutant conversion, Separation and Purification Technology. 100 (2012) 22-29.

[53] U. Von Gunten, J. Hoigne, Bromate formation during ozonation of bromide-containing waters: Interaction of ozone and hydroxyl radical reactions, Environmental Science and Technology. 28 (1994) 1234-1242.

Supplementary Information

Novel pre-treatments to control bromate formation during ozonation

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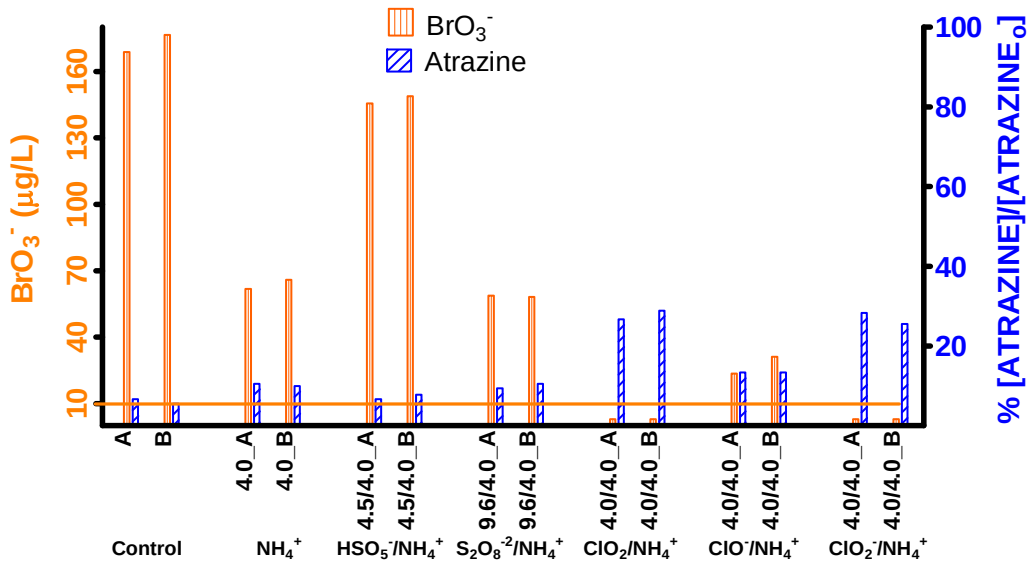
Supplementary Figures and Schemes Captions

Figure S1: Reproducibility of the experiments on BrO_3^- formation and ATR removal at the highest doses. Experimental conditions: O_3= 3.5 mg/L; Br^- = 100 μg/L; ATR_o= 200 μg/L; NH_4^+ = 4, mg/L; $[NH_4^+]/[Br^-]$ = 178; [Ox] =60 μM; $[Ox]/[Br^-]$ =48.

Table S1: Cost of pre-treatments based on the optimum oxidants (Cl_2, ClO_2, ClO_2^-, and MnO_4^-) and NH_4^+ concentrations

Materials and Methods:

Chlorine Dioxide: For the preparation of 1L of ClO_2, 400 mL of Milli-Q water were mixed with 25 mL of HCl (9%) and 25 mL of NaClO2 (7.5% =75g/L). The glass bottle was covered with aluminum foil and the cap was placed carefully on the top allowing space for gas release. The next day milli-Q water was added to complete the volume at 1000mL. The concentration of the stock was measured photometrically with a HACH LANGE DR2800.



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After obtaining the data depicted in Figure 1 it was decided to verify the reproducibility of the experiments. Therefore, the experiments with the highest level of oxidant concentration ($[NH_4^+]/[Br^-]$ = 189, [Oxidant] = 60 µM and O_3 = 3.5 mg/L), were repeated in two separate batches (A and B) (Figure S1). It is evident from Figure S1, that both BrO_3^- and atrazine concentrations are very close and in some cases the error between the measurements was lower than the error of the analytical method. The data were also statistically analyzed by performing t-testing at 95% confidence, which confirmed that the data do not vary statistically. This means that the way the experiments were conducted is generating reliable and reproducible results.

Table S1: DTU-tap water analysis

Expanded water control
With organic micro pollutants
Analysis Report Lyngby Waterworks April 29, 2008

Parameter			Result	Water Quality Requirements 1)	Method	St
Platinum	Pt	mg/l	4	5	DS/EN7887	5%
Turbidity		FTU	0,15	0,3	DS/EN27027	5%
pH		pH	7,65	7,0-8,5	DS287	
Conductivity		mS/m	82		DS/EN27888	2%
Evaporation residue		mg/l	485	1500	DS204	5%
NVOC	C	mg/l	1,8	4	SM5310	5%
Calcium	Ca^{2+}	mg/l	111		DS/EN14911	3%
Magnesium	Mg^{2+}	mg/l	17	50	DS/EN14911	3,50%
Total Hardness		^{o}dH	19,4		DS/EN14911	3,50%
Sodium	Na^{+}	mg/l	32	175	DS/EN14911	3%
Potassium	K^{+}	mg/l	4,2	10	DS/EN14911	3%
Ammonium	NH_4^{+}	mg/l	0,05	0,05	SM 418B	4%
Iron	Fe	mg/l	0,02	0,1	DS225	4%
Manganese	Mn	mg/l	0,005	0,02	DS227	5%
Bicarbonate	HCO_3^{-}	mg/l	332		DS/EN9963-1	2%
Chloride	Cl^{-}	mg/l	71	250	DS/EN10304	1,50%
Sulphate	SO_4^{2-}	mg/l	46	250	DS/EN10304	1,50%
Nitrate	NO_3^{-}	mg/l	2,6	50	DS/EN10304	2,50%
Nitrite	NO_2^{-}	mg/l	0,01	0,01	DS6777	1,50%
Phosphorus, total	P	mg/l	0,02	0,15	DS292	5%
Fluoride	F^{-}	mg/l	0,35	1,5	DS/EN10304	3%
Oxygen	O_2	mg/l	8,5		DS2205	5%
AGGR. Carbon dioxide	CO_2	mg/l	2	2	DS236	2%

1) See Statutory Order no. 871 dated 21 September 2001

* Outside of accreditation

! Water quality requirements not met

m.l.: measurable limit

St??????

Udvidet drikkevandskontrol
Med organiske mikroforureninger
Analyserapport Lyngby Vandværk 29. april 2008

Fysisk-kemisk undersøgelse			Resultat	Vandkvalitets-krav 1)	Metode	St
Farvetal	Pt	mg/l	4	5	DS/EN7887	5%
Turbiditet		FTU	0,15	0,3	DS/EN27027	5%
pH		pH	7,65	7,0-8,5	DS287	
Ledningsevne		mS/m	82		DS/EN27888	2%
Inddampningsrest		mg/l	485	1500	DS204	5%
NVOC	C	mg/l	1,8	4	SM5310	5%
Calcium	Ca++	mg/l	111		DS/EN14911	3%
Magnesium	Mg++	mg/l	17	50	DS/EN14911	3,5%
Hårdhed total		°dH	19,4		DS/EN14911	3,5%
Natrium	Na+	mg/l	32	175	DS/EN14911	3%
Kalium	K+	mg/l	4,2	10	DS/EN14911	3%
Ammonium	NH4+	mg/l	<0,05	0,05	SM 418B	4%
Jern	Fe	mg/l	0,02	0,1	DS225	4%
Mangan	Mn	mg/l	<0,005	0,02	DS227	5%
Bicarbonat	HCO3-	mg/l	332		DS/EN9963-1	2%
Klorid	Cl-	mg/l	71	250	DS/EN10304	1,5%
Sulfat	SO4--	mg/l	46	250	DS/EN10304	1,5%
Nitrat	NO3-	mg/l	2,6	50	DS/EN10304	2,5%
Nitrit	NO2-	mg/l	<0,01	0,01	DS6777	1,5%
Fosfor , total	P	mg/l	<0,02	0,15	DS292	5%
Fluorid	F-	mg/l	0,35	1,5	DS/EN10304	3%
Ilt	O2	mg/l	8,5		DS2205	5%
Aggr. Kuldioxid	CO2	mg/l	<2	2	DS236	2%

1) Se Miljøministeriets bekendtgørelse nr. 871 af 21. september 2001

* Uden for akkreditering

! Vandkvalitetskrav ikke overholdt

i.m.: Ikke målelig

St: Total fejl

Table S2: Cost* of pre-treatments based on the optimum oxidants (Cl_2, ClO_2, ClO_2^-, and MnO_4^-) and NH_4^+ concentrations

Treatment	O_3 dose g/m^3	Oxidant	Oxidant dose g/m^3	NH_4^+ dose g/m^3	Cost of oxidant €/m^3	Cost of NH_4^+ €/m^3	Pre-Treatment Cost c€/m^3
Pretreatment with NH_4^+				1	N/A	0,0022	0.22
Pretreatment with NH_4^+-Cl_2		Cl_2	4	4	0,008	0.0089	1,69
Pretreatment with NH_4^+-MnO_4^-	3.5	MnO_4^-	2.4	0,4	0,038	0.0009	3.84
Pretreatment with NH_4^+-ClO_2^-	3.5	ClO_2^-	0.6	0,4	0,007	0.0009	0.76
Pretreatment with NH_4^+-ClO_2	3.5	ClO_2	0.6	0,1	0,021	0.0002	2.12

*Based on German market prices for bulk chemicals as given by relevant suppliers obtained August 2010.